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PICOSECOND DYNAMICS OF I(2) PHOTODISSOCIATION.(U)

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P. Bado, P.H. Berens, J.P. Bergsma, S.B. Wilson and K. R. Wilson

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## PICOSECOND DYNAMICS OF $I_2$ PHOTODISSOCIATION

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### 1. Introduction

While liquid solution reactions are much more important in chemistry, gas phase reactions are much better understood. Given the central importance of solution reactions to inorganic, organic, industrial and biochemistry, it is rather surprising that, as yet, there is not a single such reaction whose molecular dynamics are understood in detail. Theoretical and experimental evidence already makes clear that much of the important molecular dynamic action in solution reactions occurs on the picosecond and subpicosecond time scales. The dihalogen photodissociation and recombination reactions,  $X_2 + h\nu \rightarrow X + X \rightarrow X_2$ , involving the simplest possible molecular reactants and products, diatomics, and in rare gas solution involving only two elements, seem excellent candidates for study.

### 2. Theory

The first deterministic theoretical study of the molecular dynamics of reactions was by BUNKER and JACOBSON[1], who computed the classical trajectories for  $I_2$  in  $CCl_4$  solvent represented by 26 spherical, structureless particles in a specular cube. MURREL, STACE and DAMMEL[2] modelled the photodissociation of  $I_2$  in dense inert gases,  $I_2$  plus 22 gas atoms in a spherical, soft-walled container. We have similarly modelled  $I_2$  plus 50 Xe atoms at liquid density in truncated octahedral periodic boundary conditions[3,4], computing the photodissociation, solvent caging, atomic recombination and vibrational energy decay to the solvent from the new  $I_2$  molecule, as shown in Fig. 1. The conclusion of all three molecular dynamic studies is that geminate recombination is usually a very fast process, over within a few picoseconds. An important caveat, and a weakness in these theoretical studies, is that the process whereby the I atoms dissociating on an excited state potential surface refund the ground state surface on which they recombine is not well understood, and is therefore handled in these calculations by arbitrary assumptions which may be incorrect. If so, the real time for geminate recombination may be longer than the few picoseconds calculated.

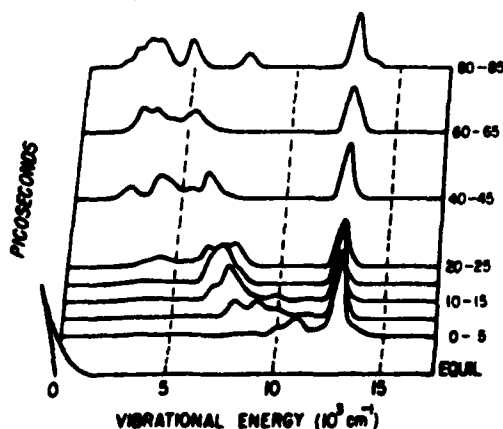


Fig. 1. Time evolution in liquid Xe solution of  $I_2$  vibrational energy during reaction sequence of photodissociation (at time zero), solvent caging of some of the recoiling I atoms, radical recombination, and vibrational loss to solvent. Also shown is the equilibrium Boltzmann vibrational energy distribution before photodissociation. The vibrational energy distribution already bifurcates into two branches within the 0-5 ps period, the higher one corresponding to those I atom pairs which have escaped the cage and whose minimum energy is the  $I_2$  dissociation energy, and the lower one corresponding to recombined  $I_2$  progressively losing vibrational energy to the solvent.

In addition, theoretical calculations by NESBITT and HYNES[5, 6] for  $I_2$  in rare gases and in  $CCl_4$  and by our group[3, 4] in liquid Xe indicate that the decay to the solvent of the vibrational energy in the newly reformed  $I_2$  molecule will require the order of a hundred to hundreds of picoseconds, as shown in Fig. 1, considerably slower than the time required for geminate recombination. Note that these calculations are for solvent atoms or molecules which are very weakly bound to one another, and that the vibrational relaxation might be quite different, for example, in a strongly hydrogen-bonded liquid.

From our calculated molecular dynamics, plus the potential curves and transition dipole moments, we can compute transient electronic absorption spectra[7], as shown in Fig. 2, which includes the  $A \rightarrow X$ ,  $B \rightarrow X$ , and the  $B^* 1u(^1\Pi) \rightarrow X$  transitions. A related nonmolecular dynamics spectral calculation has been carried out by NESBITT and HYNES[6]. A small quantum correction by temperature scaling, which would be exact for the coordinate distribution in the harmonic limit, is made to the equilibrium spectra which agree well with the known  $I_2$  experimental spectral points[8]. Note that spectra measured at different wavelengths follow different time histories, which can in principle be used to follow the time evolution of the vibrational energy distribution of the relaxing  $I_2$  molecules.

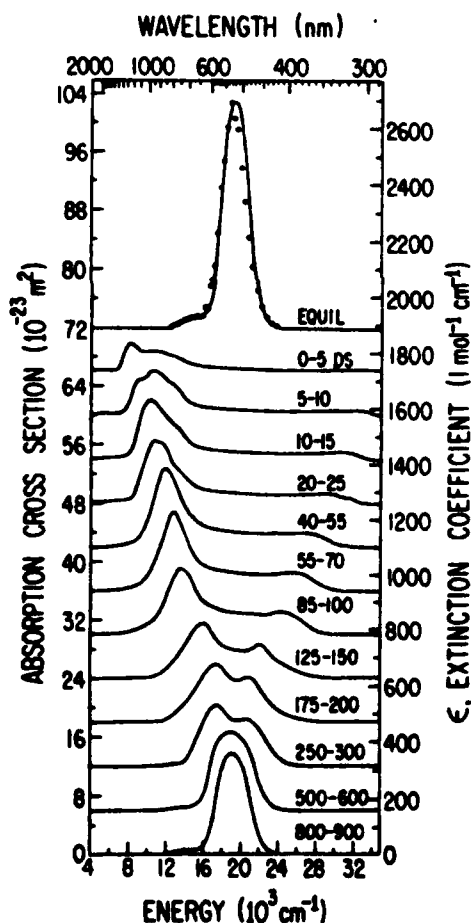


Fig. 2. Transient electronic absorption spectra computed from molecular dynamics for  $I_2$  (in Xe solution) reaction sequence of photodissociation, solvent caging, radical recombination, and vibrational decay. Time zero is the photodissociation. The top curve is the computed equilibrium spectrum before photodissociation on which are superimposed the experimental points from Tellinghuisen[8].

### 3. Experiment

The earliest picosecond experimental results were by the EISENTHAL group[9, 10], who measured the transient electronic absorption spectra after excitation at 530 nm. Decay times of  $\sim 70$  ps for  $I_2$  in hexadecane and  $\sim 140$  ps in  $CCl_4$  were observed. Subsequently these studies were extended by the EISENTHAL group to  $I_2$  in aromatic solvents[11] which are believed to form complexes with  $I$

atoms, and by LANGHOFF[12] who observed  $I_2$  photodissociation in several weakly associated liquids, finding decay times in the  $\sim 100$ - $150$  ps range. More recently, KELLEY and RENTZEPIS[13] have observed  $I_2$  photodissociation in fluid and liquid Xe with a decay time of  $\sim 40$  ps, as well as in  $CCl_4$ , and similar experiments have been carried out by the PETERS group[14]. All of the above studies used second harmonic Nd pump light at  $\sim 530$  nm, which, at least in the gas phase, results in excitation largely to the bound  $B\ 0_v^+(^3\Pi)$  state which presumably predissociates, but may absorb another photon in the meantime[15,16]. A delay of  $\sim 20$  ps between excitation and the maximum in the absorption curve has been attributed to absorption from the B state[9, 13, 17]. Thus, the linking of these experimental transient spectra to the molecular dynamics of the  $I_2$  photodissociation and recombination reaction is made difficult by the probable presence of the additional processes of B state predissociation and absorption. We have recently reported[3] transient absorption for  $I_2$  excited using an  $Ar^+$ -dye (DCM) synchronously pumped source at 710 nm into the dissociative A state, thus avoiding the problem of predissociation. In order to achieve the sensitivity needed to detect the very weak[8]  $I_2$  A state absorption, we use a multiple modulation system[18] based on the discovery by HERITAGE[19] and LEVINE and BETHEA[20,21] that the noise in  $Ar^+$  synchronously pumped dye lasers falls off by several orders of magnitude in going from the audio to the radio frequency region. We modulate the pump and probe beams at two different radio frequencies and detect at the difference frequency, using inexpensive and readily available radio amateur equipment[18]. In addition, we audio modulate the pump beam and synchronously detect at that frequency. Decay times are shown in Fig. 3. We suggest the hypothesis that vibrational decay might be expected to be faster for the more strongly hydrogen-bonded solvents which are expected to have a greater spectral mode density in the range of  $I_2$  vibrational frequencies. All the above experimental measurements suffer in interpretation from the rather weak connection between molecular dynamics and electronic absorption, which is further complicated by the possible presence of  $I_2$ -solvent,  $I$ -solvent, and  $I_2-I_2$  complexes.

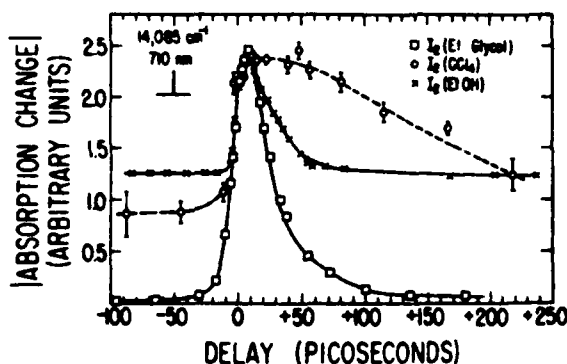


Fig. 3. Experimental transient electronic absorption spectra for  $I_2$  in ethylene glycol (0.2 molar,  $1.3 \times 10^{-2}$  mole fraction), in ethyl alcohol (0.33 molar,  $1.9 \times 10^{-2}$  mole fraction), and in  $CCl_4$  (0.096 molar,  $9.3 \times 10^{-3}$  mole fraction). All the spectra are for perpendicular orientation of linearly polarized pump and probe beams.

#### 4. Discussion and Conclusion

In summary, two hypotheses have been advanced: i) that geminate recombination for  $I_2$  is relatively slow and thus accounts for the observed range of transient absorption decay times and ii) that geminate recombination is relatively fast and that vibrational decay times to reach vibrational levels with higher absorption instead account for the observed transient absorption decay times. At the present time, the available theoretical and experimental tools have not been sufficiently powerful to cleanly disprove either or both of these hypotheses.

Improvements in both theoretical and experimental tools should lead to more stringent tests. On the theoretical side, molecular dynamics and spectral calculations can certainly be extended to a variety of different solvents, and to different pump photon energies and thus different  $I$  atom recoil energies. In addition, different assumptions as to the mechanism for relaxation to the ground state potential curve can be tried out. Transient electronic absorption measurements suffer from the intrinsic limitation of a weak connection to molecular dynamics. In contrast, transient Raman spectra can directly reveal, for example, rotational and vibrational periods in the evolving reactants and products. We have computed such transient spectra [3,4] for this reaction sequence. The

equivalent resonance Raman spectra can also be calculated and they also will reveal much of the underlying molecular dynamics, possibly including upper state recurrence times[22]. Thus Raman spectra could provide a definitive test of the above hypotheses.

It is surprising, but true, that for no chemical reaction in solution, not even for one as simple and as well studied as  $I_2$  photodissociation and recombination, are the detailed atomic motions by which it occurs yet known. Even such basic aspects are not certain as the order of magnitude of the time required for caging and geminate recombination, and whether a direct deterministic or a stochastic diffusional approach to geminate recombination is most appropriate.

This situation may soon change, as there is now a four order of magnitude time range,  $\sim 100$  fs to 1 ns, over which molecular dynamic calculations and short light pulse experiments can overlap. Transient infrared, Raman and electronic absorption spectra all reflect the underlying molecular dynamics of chemical reactions and can provide an interface at which theory and experiment may meet. By comparing transient spectra computed from molecular dynamics with the equivalent measured spectra, one can hope to discover the microscopic dynamics by which many chemical processes occur.

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